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THE LONG-TERM WEATHERING OF HEAVY CRUDE OILS: EXPERIMENTAL MEASUREMENTS AND DEVELOPMENT OF MODELS

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ABSTRACT

A research project is described in which observations and measurements are being made of the long term weathering processes to which heavy crude oils are subject. Experimental systems have been developed to expose the oil under controlled conditions to (i) evaporative weathering, (ii) dissolution weathering, and (iii) combined processes. The analytical systems are described, and an approach to modelling the data is suggested. Of particular interest is the formation of a weathered "crust" which appears to retard the weathering processes

INTRODUCTION

The Incentive

Numerous experimental studies and observations of real spill behaviour have shown that when conventional and heavy crude oils and petroleum products are spilled in the marine environment they are subject to a number of processes collectively termed "weathering", which cause profound changes in the oils' physical and chemical properties and composition. These processes include evaporation, dissolution, photolysis, formation of oil-in-water emulsions and water-in-oil emulsions, and adherence to the oil of organic matter and mineral particles present in the water column.

As weathering proceeds, the oils usually become denser, and their viscosity increases, and ultimately the oil masses may form semi-solid droplets or tar balls which float in a near-submerged state at the water surface. This material may persist indefinitely on the sea surface, or become stranded on shore, or sink and become incorporated into sediments. It is important to determine which types of oils, under which conditions, are subject to which type of behaviour. Whereas most experimental measurements are being made over the short-term, it is increasingly obvious that there is a need to predict long term behaviour of oil because this oil may drift appreciable distances from the source of the spill. A convenient review of these issues can be found in a recent report by Lee et al. (1989).

The purpose of this study is to design and test various methods by which long-term weathering phenomena can be investigated, observed and if possible quantified. The approach has been to isolate and quantify on an individual basis two weathering processes which are believed to be of particular importance.

Experimental Approach

First is evaporation which can cause appreciable density and viscosity increases. We have thus sought to devise an experimental approach, or protocol, for measuring the extent to which hydrocarbons will evaporate from oil, and in doing so identify the hydrocarbons which have evaporated. This is done in the hope that the protocol may be useful for routine characterization of oils which may be produced or transported in the marine or aquatic environment.

The second process is dissolution which is less important from the viewpoint of loss of mass by the oil, but is critically important for assessment of toxicity to aquatic or marine organisms. Again, we have sought to develop an experimental protocol whereby oils may be subjected to controlled dissolution conditions, and the dissolved and remaining oil identified and quantified.

A third aspect has been to devise a relatively simple laboratory system for measurement and observation of the long-term weathering of crude oils on a water surface. The oil is thus subjected to dissolution, evaporation and photolysis. The aim has been to simulate, as realistically as possible in the laboratory, conditions which occur at the ocean surface, and thus elucidate how a particular oil will be expected to behave as a result of combined weathering processes.

A problem inherent in this latter aspect is that it has been observed that as an oil weathers it may form a protective skin or crust consisting of high density, high viscosity material. This material, possibly altered chemically as a result of photolysis, protects the underlying or interior oil from further exposure to evaporation or dissolution. It is not clear which oils are susceptible to this phenomenon, and at which stage of weathering it occurs. Thus the simulation of evaporation, dissolution and photolysis simultaneously is necessary to gain an appreciation of each oil's characteristic behaviour.

A final aspect which is investigated in this study is the formation of water-in-oil emulsions. Previous reviews have been presented by Payne and Phillips (1985), and Mackay (1987). These emulsions are generally of high viscosity and high water content, and they profoundly affect oil behaviour and the feasibility of clean-up. Accordingly, a smaller experimental effort is being devoted to establishing the susceptibility of the oils to emulsion formation, and the stability of these resulting oils.

Models

Ultimately, it is desirable to develop some form of mathematical modelling approach to translate laboratory results to marine environmental conditions. The general sequence of events envisaged would be that standard laboratory tests would be conducted to obtain parameter values characteristic of the oil, and especially of its susceptibility to evaporation, dissolution, photolysis and emulsion formation. A mathematical model would be fitted to the experimental data. The same mathematical model would then be used under the different conditions of oceanic exposure, but with the same parameter values, in order to estimate the changes in oil composition and properties with time.

Ideally, it should be possible in a laboratory to "accelerate time", that is, undertake oil exposure experiments over a period of perhaps 20 days in the laboratory which will simulate exposure conditions in a marine environment for perhaps 200 days. There are obvious limitations in this respect; however, in the interests of economy, it is desirable to obtain oil characteristic data in as short a period of time as possible.

Any attempt to prepare a mathematical model of oil behaviour is rendered difficult by the very complex nature of crude oils, and especially the large number of components which are of unknown structure and properties. Accordingly in this study, we have attempted to develop a novel "matrix" approach for oil characterization during long-term weathering by modifying a procedure developed in our group for characterizing the long-term weathering behaviour of oils in a soil environment (Eastcott et al., 1987). The general concept is that the oil is divided up into a number of pseudo-components, each of which has defined properties such as volatility, solubility, density, and viscosity. As the oil is weathered, there is selective removal of these components caused by exposure to evaporation or dissolution. The result is a change in the proportion of the chemicals present in the matrix, and thus a change in the overall properties of the oil. In principle, it should be possible to characterize the changing properties of oil in terms of changes in the magnitude of the elements in the matrix.

Analyses

The key problem is the development of analytical techniques which will enable the composition of the original oil, and experimentally weathered oils, to be expressed in terms of matrix elements. Gas chromatography is very convenient as a method of characterizing the volatility of crude oils, thus one dimension of the matrix should obviously be a separation of oil into rows which consist of elements similar in volatility. It is desirable to separate the oil into matrix columns based on solubility, but this is more difficult. The first obvious approach is to subject a sample of the oil to dissolution under controlled conditions, and measure the amount of oil dissolved. This has been investigated as part of this project. A second approach is to separate the oil into classes of hydrocarbons such as alkanes, aromatics and polars which are known to have widely different solubility characteristics. If it was possible, for example, to assign a common solubility to the aromatics which lie in a specified volatility range then this approach can be used to provide a series of columns corresponding to oil components of different chemical structure. A third and attractive possibility, if it is feasible, is to subject oil fractions to HPLC analysis and separate the oil into solubility classes relying on the relationship between HPLC retention time and water solubility, or more precisely the water to stationary phase partition coefficient. This can be done using either conventional or reversed phase HPLC techniques. This HPLC approach has the advantage in that it is fast and routine, and could introduce considerable economies of time into the determination. However, it has not been to our knowledge successfully applied in this context although it has been used by various workers to estimate octanol-water partition coefficients for hydrophobic organic substances.

Accordingly, we have approached this problem by attempting all three methods with a view to establishing the preferred one.

In the balance of this paper, we describe the oils which are currently being tested, the experimental procedures which have been developed and are being used, and present some preliminary results. Full results will be published by Environment Canada in a forthcoming EE Series Report.

EXPERIMENTAL

The heavy crude oils were supplied by Environment Canada and the US Minerals Management Services. EPS standard oil was also used as to help develop an experimental protocol whereby heavy crude oils may be subjected to evaporation and dissolution conditions.

The physical-chemical properties of the heavy crude oils are listed in Table 1, and their gas chromatograms are shown in Figure 1. Table 2 gives the composition of the original oils using open column chromatography.

Table 1. Properties of Heavy Crude Oils and Residual Fuels

Property	California Crude API 15	California Crude API 11	Bunker C Fuel Oil	Cold Lake Bitumen	EPS
API Gravity	13.2	10.3	12.3	9.8	
Density (g/cm^3) @ 22 +/- 2°C	0.9681	0.9779	0.9712	0.9851	0.836
Viscosity (cp) @ 15°C	3.1e4	3.4e4	4.8e4	2.4e5	7.09*
Solubility (mg/L)					
d.d H_2O	25.7	11.3	4.23	0.26	34.5
salt H_2O**	14.7	9.74	1.95	0.13	

*3.0 % NaCl in salt H_2O.
**measured at 20°C.

Table 2. Hydrocarbon Analysis by Open Column Chromatography

Composition	California Crude API 15	EPS
Saturates	48.3	75.5
Aromatics	21.8	18.6
NSO compounds	5.1	3.63
Asphaltene	24.8	2.26

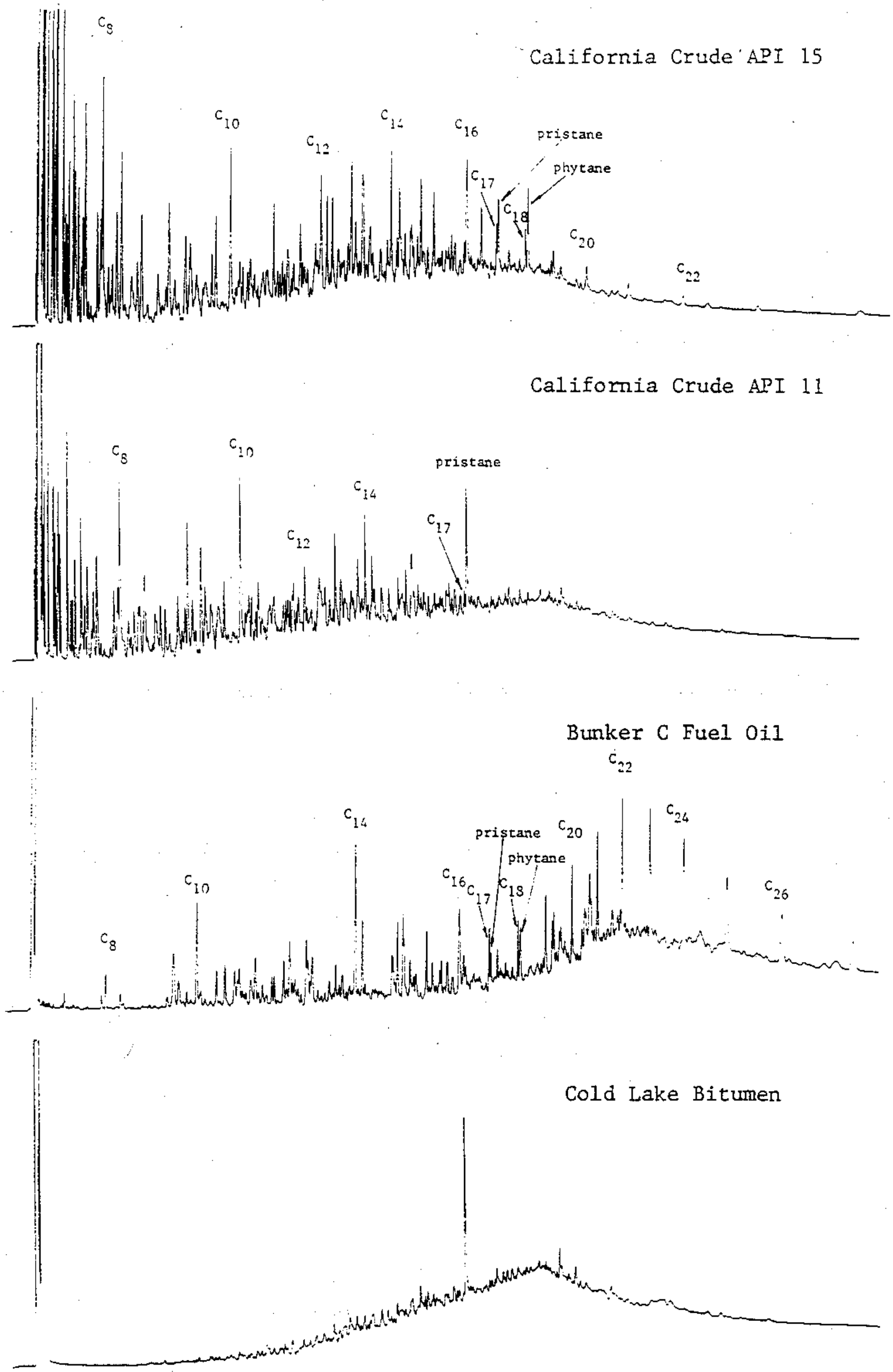

Figure 1. Gas chromatograms of heavy crude oils and residual fuels.

Oil Weathering

Evaporation

There are several experimental methods for oil evaporation. One technique was to use a modified version of the gas stripping apparatus (Stiver and Mackay, 1984) which is shown in Figure 2A. A 250-mL graduated cylinder was fitted with a lid from which a glass tube was extended to the bottom of the container. The lower end of the inlet tube was enclosed except for several pinholes through which air was bubbled. Two gas traps were connected in series to the outlet of the cylinder. These vessels were similarly constructed, but the inlet tubes were open at the bottom. The gas traps were cooled with liquid nitrogen.

Air was supplied from the laboratory supply, and a Scientific Wet Test Meter was used to measure the cumulative air flow through the gas stripping system.

The graduated cylinder was filled with a known mass and volume of oil, and air was bubbled through the oil at a rate of 400 mL/min through the system. The air supply was periodically stopped, and at which time, the remaining mass and volume of the crude oil in the cylinder were measured as a function of the cumulative volume of air which flowed passed. In addition, oil samples were analyzed by gas chromatography to quantify the extent to which hydrocarbons were evaporated from oil. The compounds stripped from the oil were recovered by the gas traps and analyzed by GC. The recovery efficiency of the evaporated hydrocarbons averaged 90 %. Measurements were thus made of the weathered oils' changing composition, amount, and properties such as density.

A second more rapid method of weathering oil by evaporation was to use a rotating mesh disk apparatus which is illustrated in Figure 2B. Appropriate amounts of oil were applied to PeCap^R polyester mesh disks (Tetko Inc.) of 60 mm diameter. These oil-covered disks were secured to the rotating device in which the continuous circular movement of the apparatus prevented the loss of oil by dripping from the mesh disks. The entire system was placed in a dark fumehood, and subjected to turbulent air flow. The effective air flow rate for the system can be determined by comparison of oil composition data with those obtained from the air stripping experiment. With this method, there is a substantially increased rate of evaporation, and density measurements are easily made.

To further accelerate the evaporation process, distillation or tray evaporation can be used, but the distillation will give different compositional changes from the other methods because of the elevated temperature.

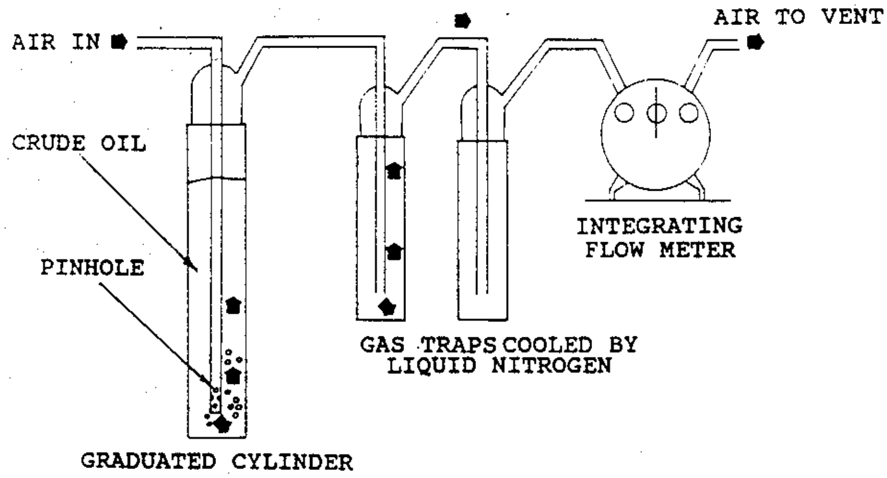

Figure 2A. Evaporation apparatus: air stripping.

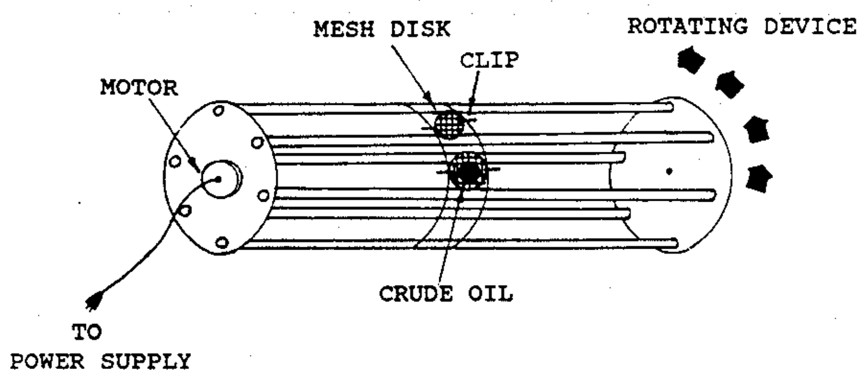

Figure 2B. Evaporation apparatus: rotating mesh disk.

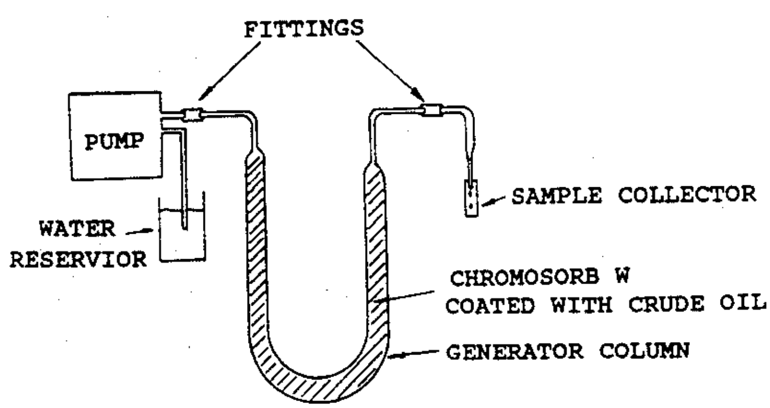

Figure 2C. Dissolution apparatus: generator column.

Dissolution

The generator column method was previously reviewed and discussed by Billington et al. (1988) and Shiu et al. (1988) for preparing solutions of single component systems and multicomponent oil systems such as crude oils. Here, we used this method to determine the identity of the dissolved hydrocarbons, and the extent to which they were dissolved as the water to oil volume was increased.

A U-tube generator column was packed with Chromosorb W (mesh size 80/100, Mansville Products Corp.) which was coated with 20 % by volume of oil. Glass wool was plugged into the ends to secure the Chromosorb W in the column. Double-distilled water was pumped with a Beckman solution metering pump through the column at a rate of 3.0 mL/min. Aqueous samples were collected at intervals and the soluble hydrocarbon concentrations analyzed by purge-and-trap GC as a function the water-to-oil volume ratio. The cumulative eluted water was measured by weighing. Two experimental runs were undertaken for each oil and were discontinued when the water-to-oil ratio reached 4100 and 10000. A schematic diagram of the generator column system is shown in Figure 2C.

After a water-to-oil volume ratio of 10000 was reached, 1.0 L of water was pumped through the remaining oil to obtain the less volatile, high-boiling point PAHs which were collected with a Waters C_{18} Sep-Pak (Waters Associates, Milford), and extracted from the cartridge with 5 mL ethyl ether. The eluent was concentrated, and analyzed by capillary GC.

The residual oils from the generator column experiments were extracted from the column with n-pentane and subjected to open column chromatography to determine the identity and amount of the undissolved hydrocarbons in the oil.

Long-term Weathering of Heavy Oils

To observe the long-term weathering of heavy crude oils on the water surface, a cylindrical container was filled with 5.0 L of distilled or salt water (3.0 wt% NaCl) on which oil was poured to form a thin slick. The water was continuously stirred with a magnetic stirrer to prevent the oil from adhering to the sides, and some of the water was replaced weekly. The apparatus was set up in the fumehood for a period of five months. Thus the oil was subjected to evaporation, and dissolution simultaneously. The changing physical characteristics of the oils were observed, and gas chromatographic analysis were performed on oil samples taken from the water surface, and eventually from denser-than-water oil globules in the water column.

Water-in-Oil Emulsion Formation

Attempts were made to form stable water-in-oil emulsions or "mousse" from California Crude API 15 with the Warren Spring apparatus using a water-to-oil volume ratio of 10:1. The water-oil mixture was rotated at 50 rpm for 6 hours. It was found that a large amount of the oil adhered to the sides of the apparatus, and any emulsion which formed proved unstable within 24 hours.

Another method of forming mousse was to use a Waring commercial blender. Approximately 15 mL of oil was added to 200 mL of water, and the mixture was blended at the low speed for 2 minutes. It was observed that an emulsion was formed, but it become unstable overnight, there being a clear separation of water from the oil. Further work is continuing to assess the stability of weathered oils.

Analysis

Gas Chromatography

Fresh and weathered oils, and their various fractions obtained from open column chromatography were analyzed by gas chromatography. The instrument used was a Hewlett-Packard GC model 5700A equipped with a flame-ionization detector. The column was a 0.75 mm ID x 50 m long glass capillary column coated with SE-30 which was supplied by Supelco Canada, Ltd. The operating conditions were as follows: the initial oven temperature was $50^{O}C$ for 8 minutes with a temperature programmed rate of $5^{O}C/min$, and a final oven temperature of $220^{O}C$ for 30 minutes. The injection sample volume was 0.5 uL with a split ratio of 50:1. The peak areas were recorded by a Shimadzu Chromatopac C-R1A integrator using the area normalization method.

Open Column Chromatography

The crude oils were separated according to their structural class by open column chromatography. The fractions obtained by this method are saturates, aromatics, and polar compounds. This analysis facilitates identification and quantification of the hydrocarbons in the oil.

The pentane-insoluble asphaltene was precipitated from the oil by addition of n-pentane (Caledon Laboratories), filtered out and weighed. The de-asphaltened oil was separated into the three fractions using the procedure described by Cook and Westlake (1976). A column was packed with a 1:1 mass ratio of silica to alumina gel. The silica (28-200 mesh) and alumina gel (type F-20, 80-200 mesh) were obtained from Sigma Chemical Co. The order of elution was saturates with n-pentane, aromatics with benzene, and then soluble polar compounds with 1:1 mixture of benzene and methanol. The fractions collected were concentrated by distillation so that little of the volatile compounds were lost by evaporation. Analysis by capillary GC yielded information on the composition and amount of each fraction in the oil.

Liquid Chromatography

An alternative method for separating oil into solubility-related fractions was normal phase liquid chromatography. The HPLC system consisted of a Waters Scientific model 510EF solvent delivery system, an U6K injector with a 2-mL sample loop, a 6-port backflush valve, and a model 401 differential refractometer. The mobile phase was HPLC-grade n-pentane, and the stationary phase was NH_2 Bondapak which was packed in a semi-preparative 2.5 cm ID x 30 cm long stainless steel column. Samples of 100 uL were injected into the system and the fractions were eluted with a flow rate of 18.0 mL/min. The peak areas were recorded with a HP-3390 integrator. The polar compounds were eluted by backflushing the flow through the column. A liquid chromatogram of a typical crude oil is shown in Figure 3. The fractions were concentrated using a micro-distillation apparatus before injecting into the GC.

Purge-and-Trap Gas Chromatography

A Hewlett-Packard model 5840A GC with a flame-ionization detector and a HP-7675A purge-and-trap sampler was used to analyze, and thus quantify the soluble hydrocarbon concentrations in aqueous samples. The column was a 0.53 mm ID x 30 m long megabore fused silica capillary column coated with DB-1 (J&W Scientific, Inc.). The oven temperature was set at $50^{\circ}C$ for 10 minutes, and then programmed to increase at a rate of $5^{\circ}C/min$ to a maximum temperature of $200^{\circ}C$ which was maintained for 20 minutes. The detector temperature was at $300^{\circ}C$. The sample volume used was between 2 to 8 mL, and the peak areas were integrated by a HP-5840A GC terminal.

The purge-and-trap technique was used to determine the aqueous solubility of crude oils. Saturated aqueous oil solutions were prepared by adding in a separatory funnel oil to water with a volume ratio exceeding 1:40. The funnel was shaken gently with a Burrell wrist action shaker for 24 hours and the mixture was allowed to settle for 48 hours before analysis.

RESULTS

A gas chromatogram of fresh EPS oil is depicted in Figure 4A. It has an abundance of low boiling, volatile hydrocarbons, and of highly water-soluble compounds such as benzene, toluene, ethylbenzene, xylenes, and

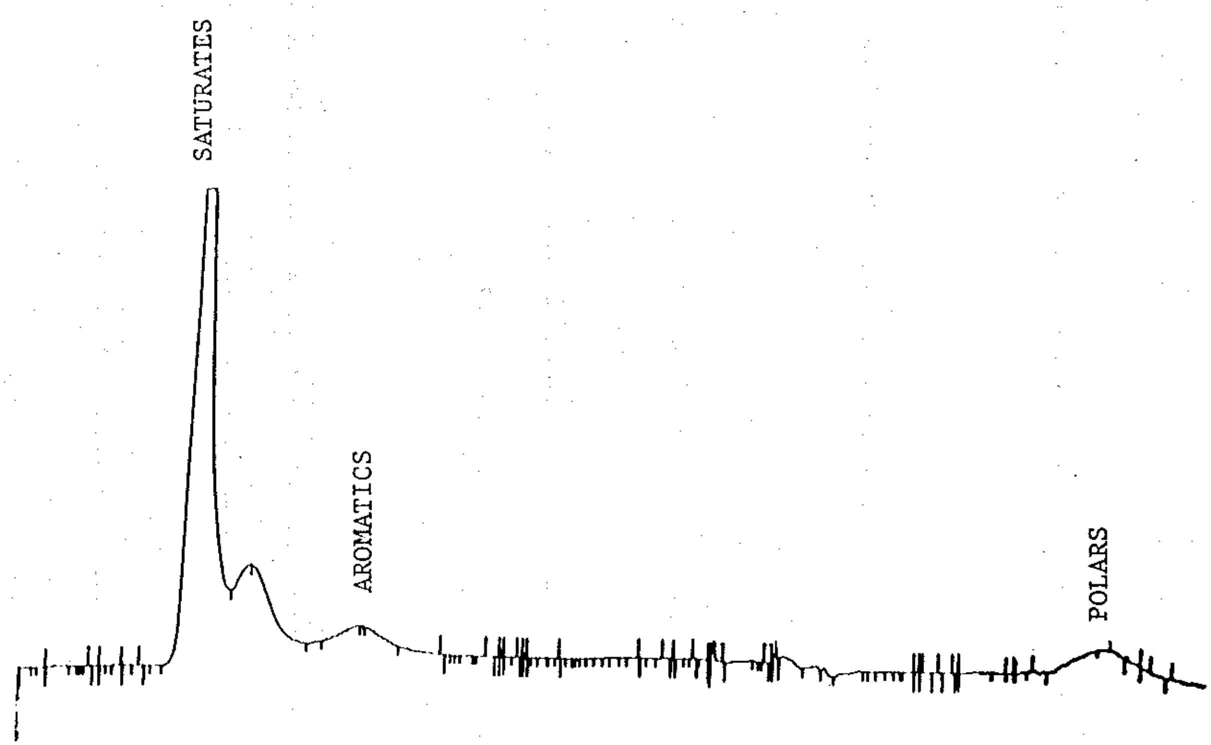

Figure 3. Liquid chromatogram of a typical crude oil.

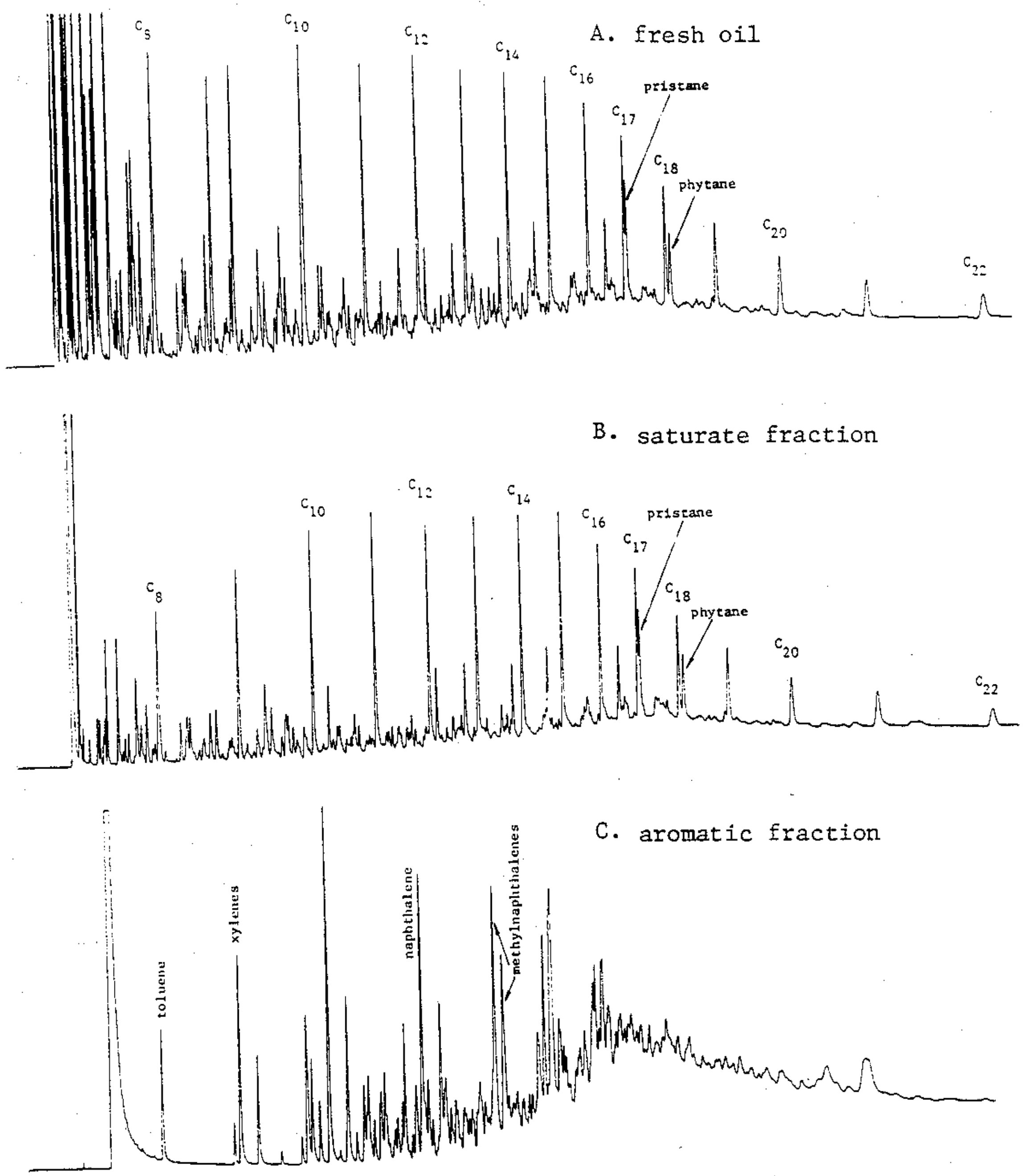

Figure 4. Gas chromatograms of fresh EPS oil and its saturate and aromatic fractions.

naphthalene as shown by Figures 4B and 4C, respectively. The saturates and aromatics were separated from the oil using asphaltene precipitation and open column chromatography.

EPS oil was chosen as the crude oil on which we performed preliminary experiments because it is easily handled, and its changing properties and composition can be clearly observed.

This oil was subjected to evaporation with the gas stripping apparatus. Figure 5 shows the sample chromatograms of the saturate and aromatic fractions for an evaporative exposure Q_E of 8060 where Q_E is the ratio of air to initial oil volumes. The extent of weathering was 24 % by volume of oil evaporated, and its density increased by from 836 kg/m^3 to 883 kg/m^3 (Figure 6). Comparison with the gas chromatogram of the fresh oil revealed the loss of the highly volatile compounds in the saturate fraction.

The rotating mesh disk apparatus worked best for viscous and dense crude oils such California Crude API 15 because they are required to be coated on mesh disks before exposing them to evaporation. A result of this method is given by Figure 7. It shows the changing composition of California Crude API 15 after 3 days of exposure or an equivalent evaporative exposure Q_E. An advantage was the increased rate of evaporation over the gas stripping method by 100 times. The larger area of oil exposed to a greater volume of air enhanced the weathering process.

Fresh EPS oil was also contacted with water in a generator column, and thus subjecting it to dissolution only. The gas chromatograms of the saturates and aromatics for Q_D (the ratio of water to oil volumes) of 10000 are shown in Figure 8. Analysis by the purge-and-trap technique revealed that the aqueous solubility of the oil decrease from 34.5 mg/L to 1.0 mg/L. The WSFs of the fresh and weathered oil are given by Figure 9 which shows that most of the volatile, water-soluble hydrocarbons such as benzene, toluene, ethylbenzene and xylenes were depleted by dissolution. Figure 10 gives the trend of the solubility of EPS oil versus the water to oil volume ratio Q_D. The solubility decreased with the depletion of the soluble aromatics.

Figure 11A is a gas chromatogram of a fresh heavy crude oil, California Crude API 15. It has a high asphaltene and tar content which accounts for its high viscosity. Its saturate and aromatic fractions (Figures 11B and 11 C) reveal that the heavy oil contains large amounts of highly volatile and soluble compounds.

California Crude API 15 was subjected to evaporation and dissolution on a water surface in long term

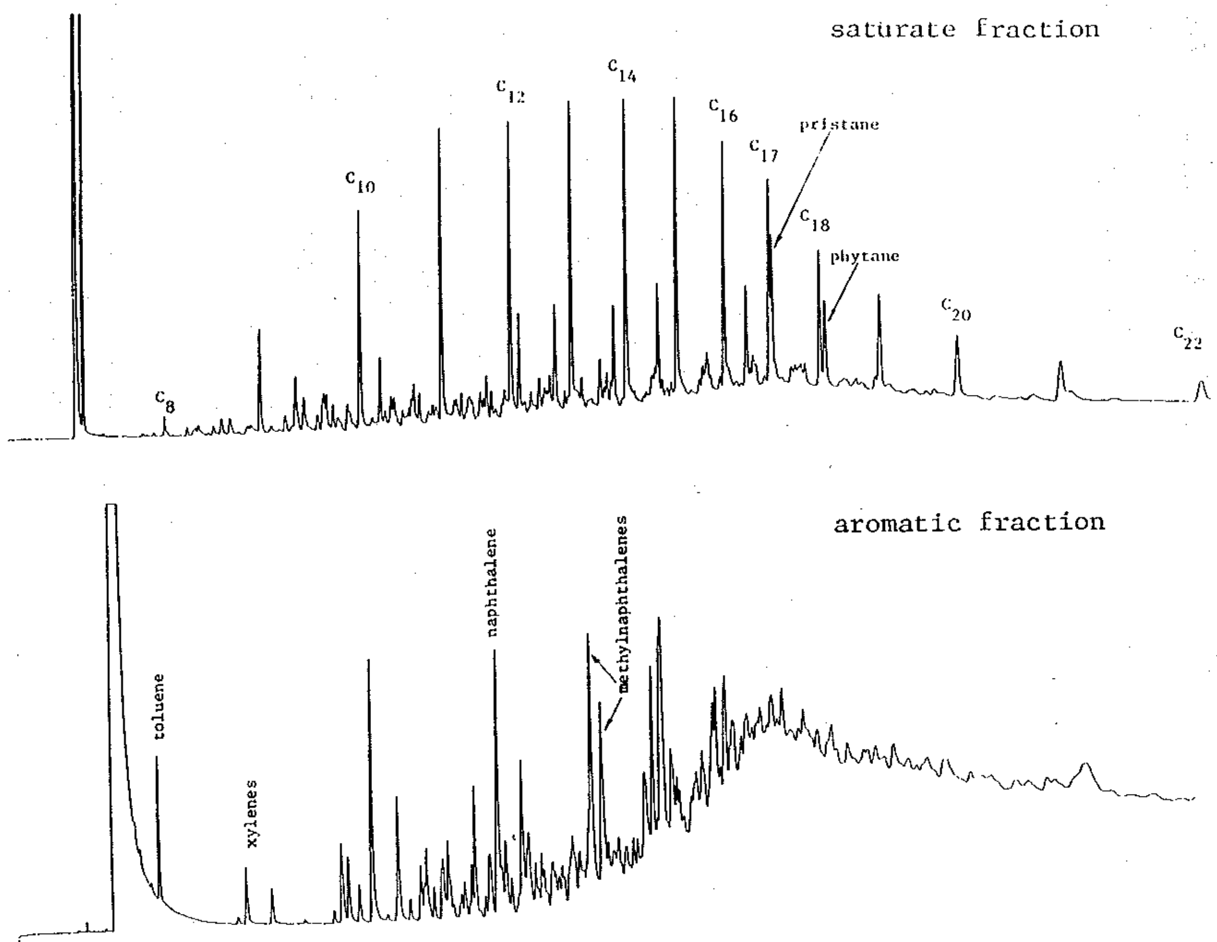

Figure 5. Saturate and aromatic fractions of EPS oil weathered using the air stripping method (Q_E=8060).

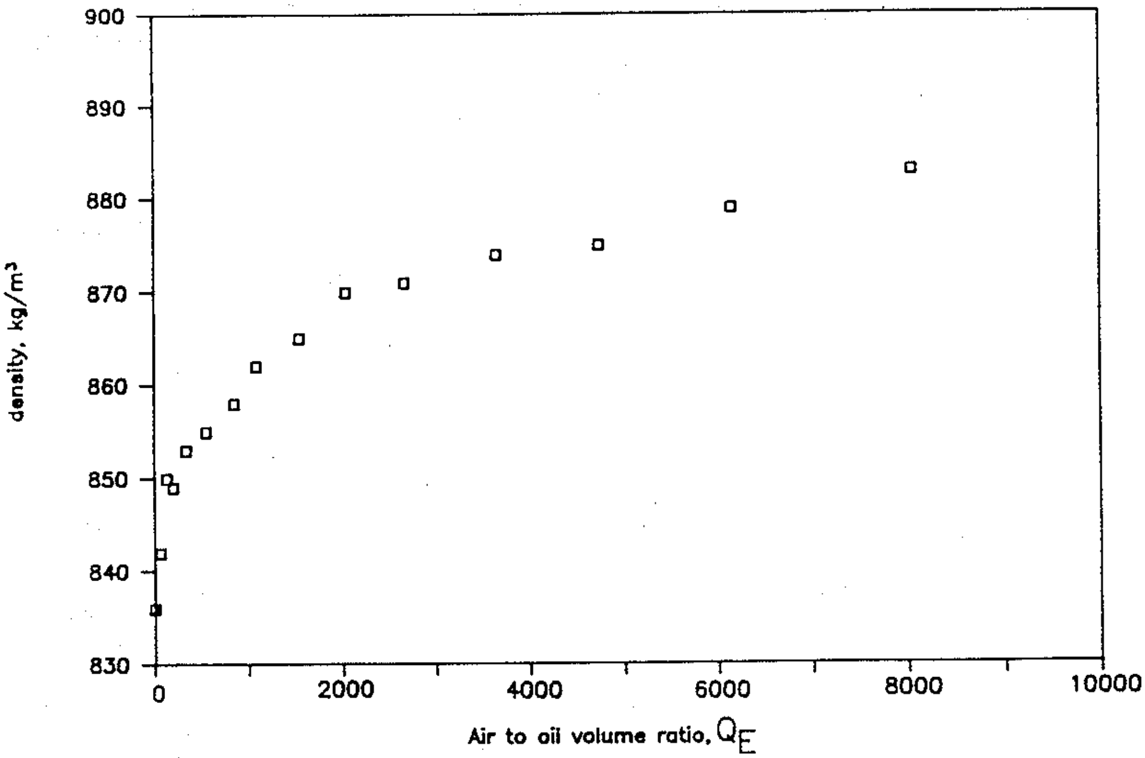

Figure 6. Density versus the air to oil volume ratio for EPS oil weathered using the air stripping method.

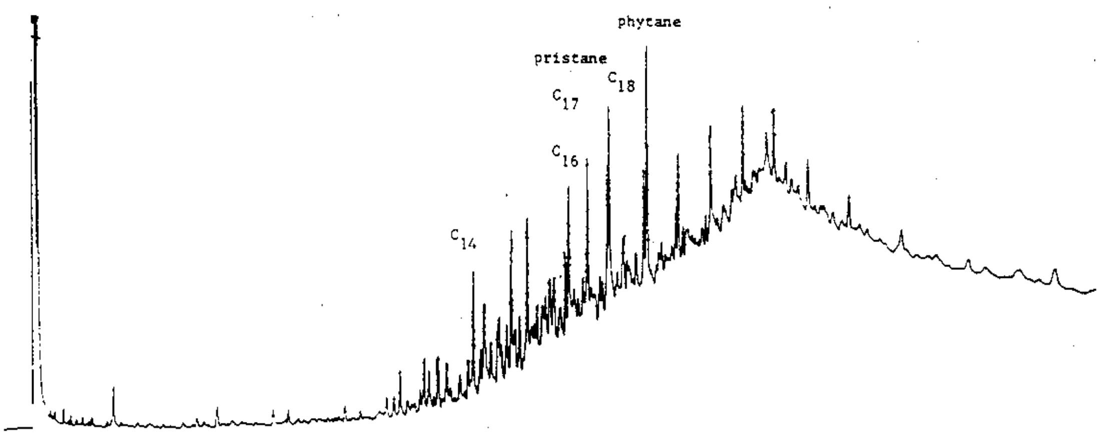

Figure 7. California Crude API 15 weathered using the rotating mesh disk method (after 3 days).

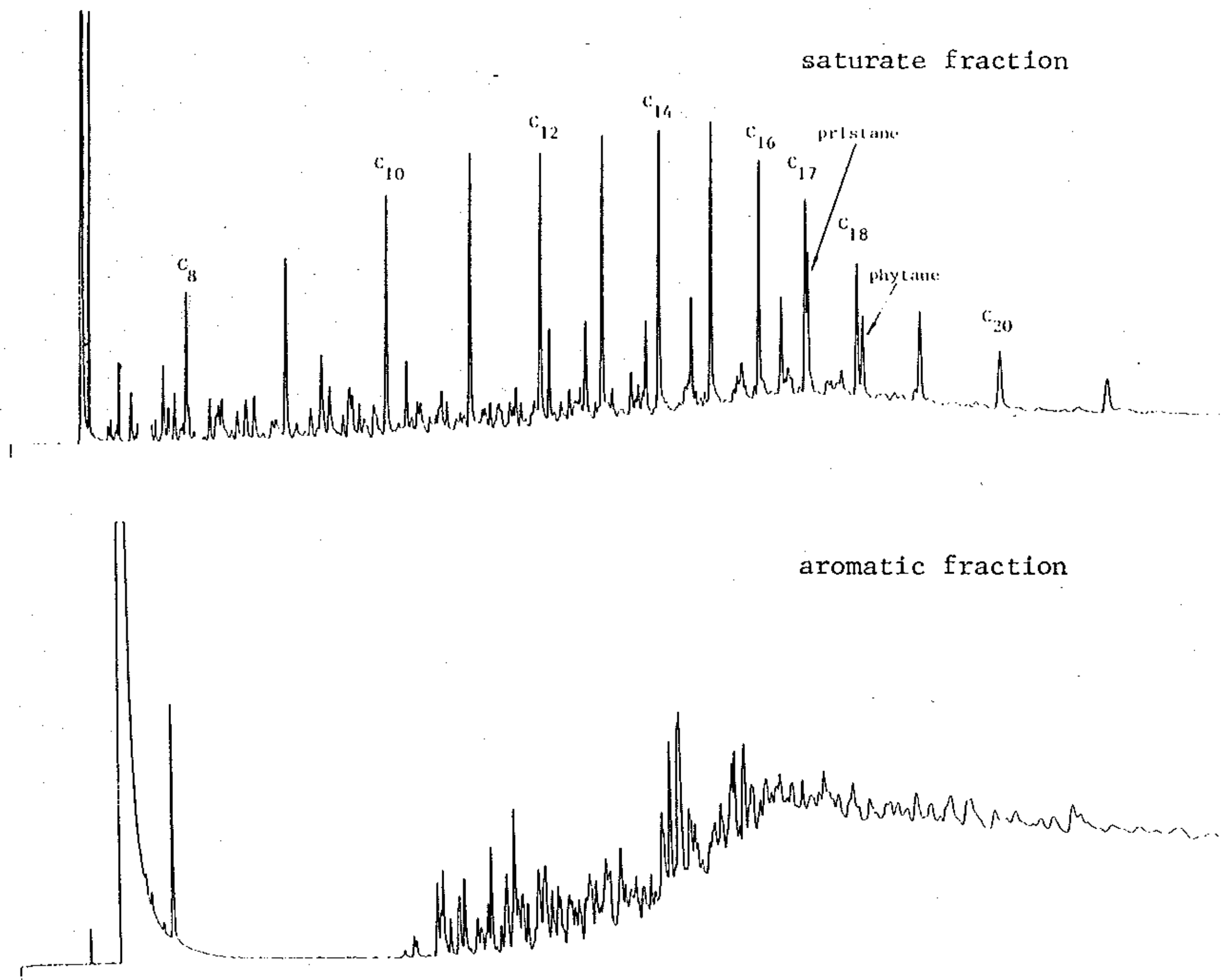

Figure 8. Saturate and aromatic fractions of EPS oil weathered using the generator column method (Q_D=10000).

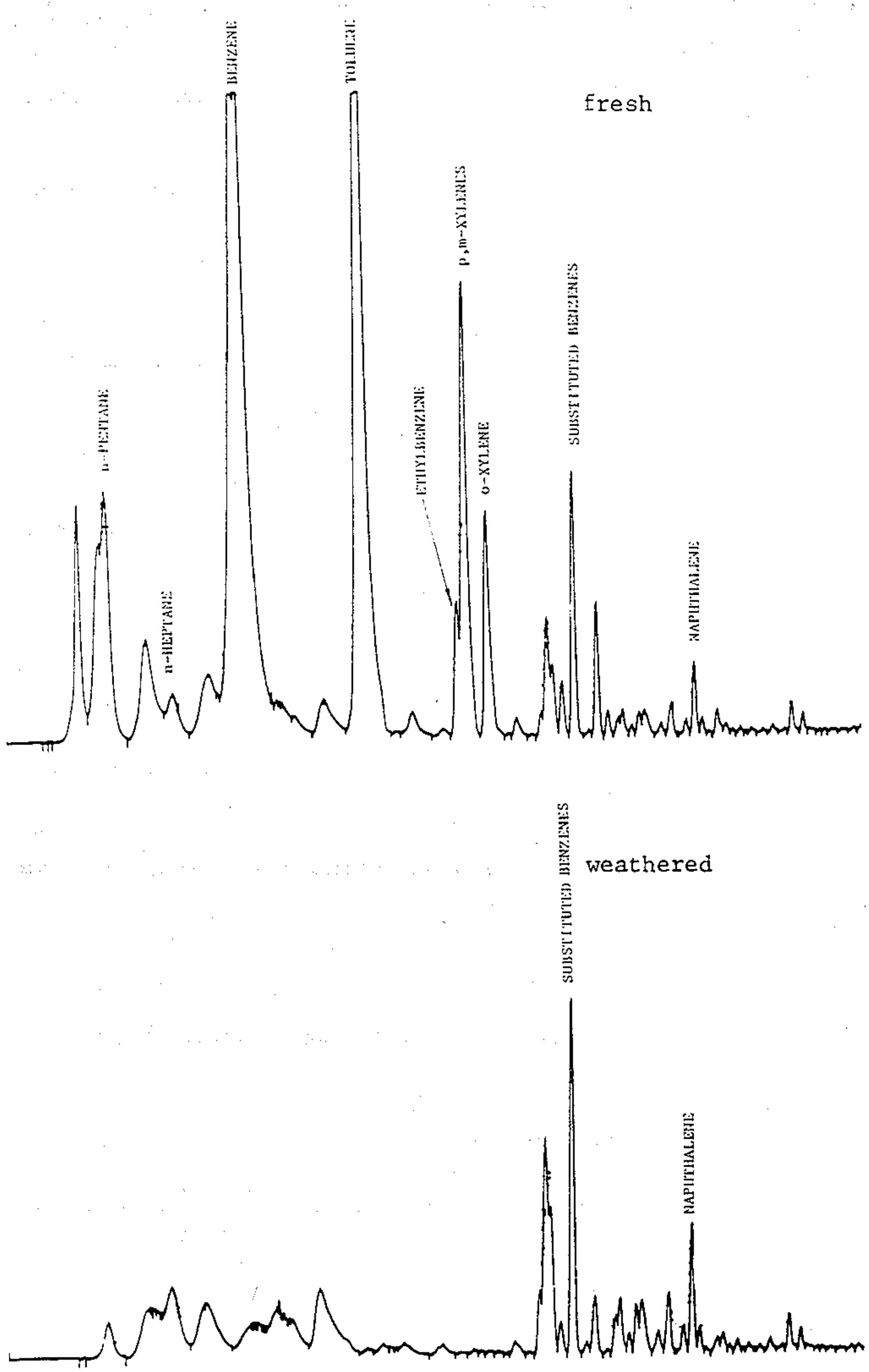

Figure 9. WSFs of fresh and weathered EPS oil.

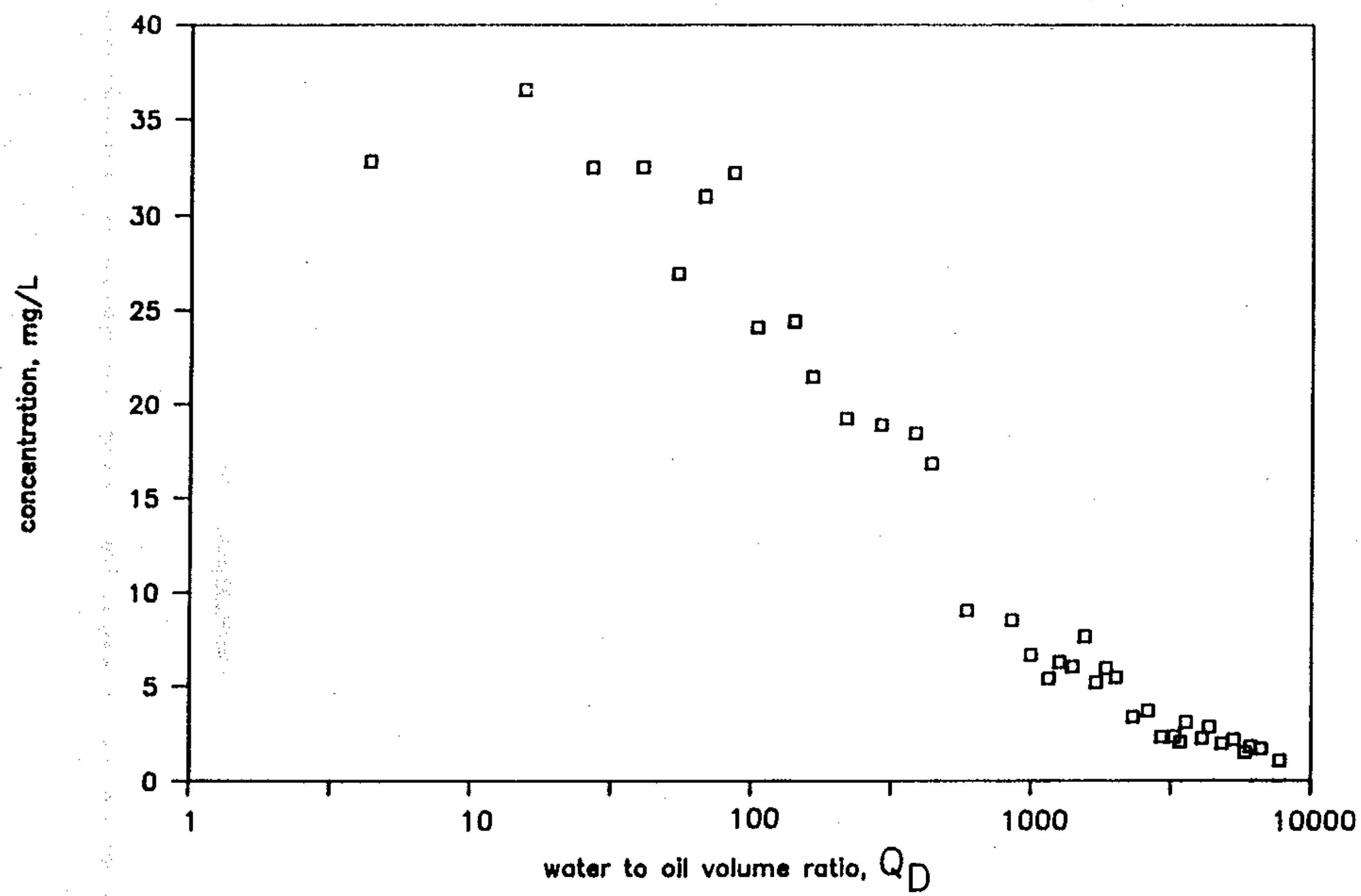

Figure 10. Aqueous solubility versus the water to oil volume ratio for EPS oil weathered using the generator column method.

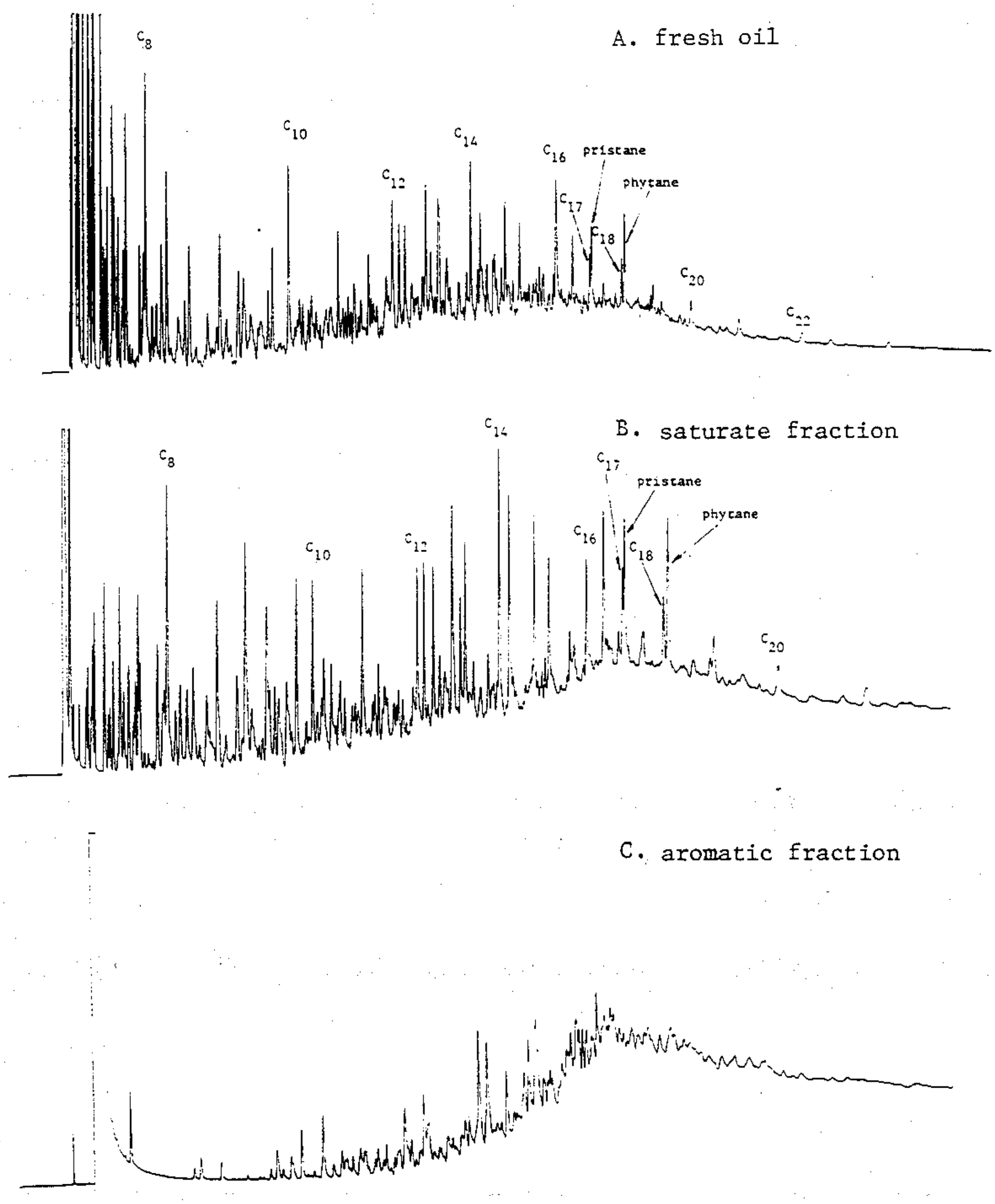

Figure 11. Gas chromatograms of fresh California Crude API 15 and its saturate and aromatic fractions.

weathering experiments. Spreading of the California Crude API 15 slick in distilled water occurred within several hours. In salt water, it spread to a lesser extent. The formation of a visible skin or crust was observed after two weeks. Tiny bubbles gradually appeared on the oil surface in both situations. After three months a 30-mm diameter oil droplet formed below the water surface and detached from the original mass in the distilled water experiment. This oil globule proved to be denser than the water because it sank into the water column. Further submergence of oil mass was observed in the next two months.

In the fifth month, an oil sample from the water surface was taken for gas chromatographic analysis. In addition, the first oil droplet was retrieved and frozen in the effort to obtain samples of the its skin/crust and interior for analysis. It proved difficult to obtain a crust sample because it was very thin, certainly less than 1 mm thick. Figure 12 illustrates the five-month weathering of the oil on the water surface and in the water column. The sunken oil was less weathered than the exposed oil on the water surface; the latter was depleted of all hydrocarbons up to C_{16}. Therefore, once submerged the oil was subjected to only dissolution which only causes a slight change in composition.

In the course of the experiments, there was no formation water-in-oil emulsions or "tar balls".

DISCUSSION

At this stage of the project, it is not possible to discuss the full results and develop conclusions, but it is useful to indicate the likely findings and the nature of the method by which the results can be modelled.

Clearly, reliable data on the extent of oil evaporation and dissolution can be obtained, but the results are specific to each oil and are not "generalizable". We envisage that the oil composition will be characterized as shown in the matrix in which the rows are of common volatility, or GC retention time, and the column classes of solubility or chemical structure. The elements to the top left will have the highest volatility and solubility. The amount in each element will be obtained by chemical analysis, that is, by GC or HPLC. Each row has a common air-oil partition coefficient K_{AO}, and each column has common solubility or water-oil partition coefficient K_{WO}. These partition coefficient are, of course, temperature dependent.

As discussed by Eastcott et al. (1987), the exposure to evaporation can be expressed as Q_E the ratio of air to oil volumes, and that to dissolution as Q_D the ratio of water to oil volumes. The fraction remaining of each element after exposure can then be approximated as

$$F = \exp(-Q_E*K_{AO}-Q_D*K_{WO})$$

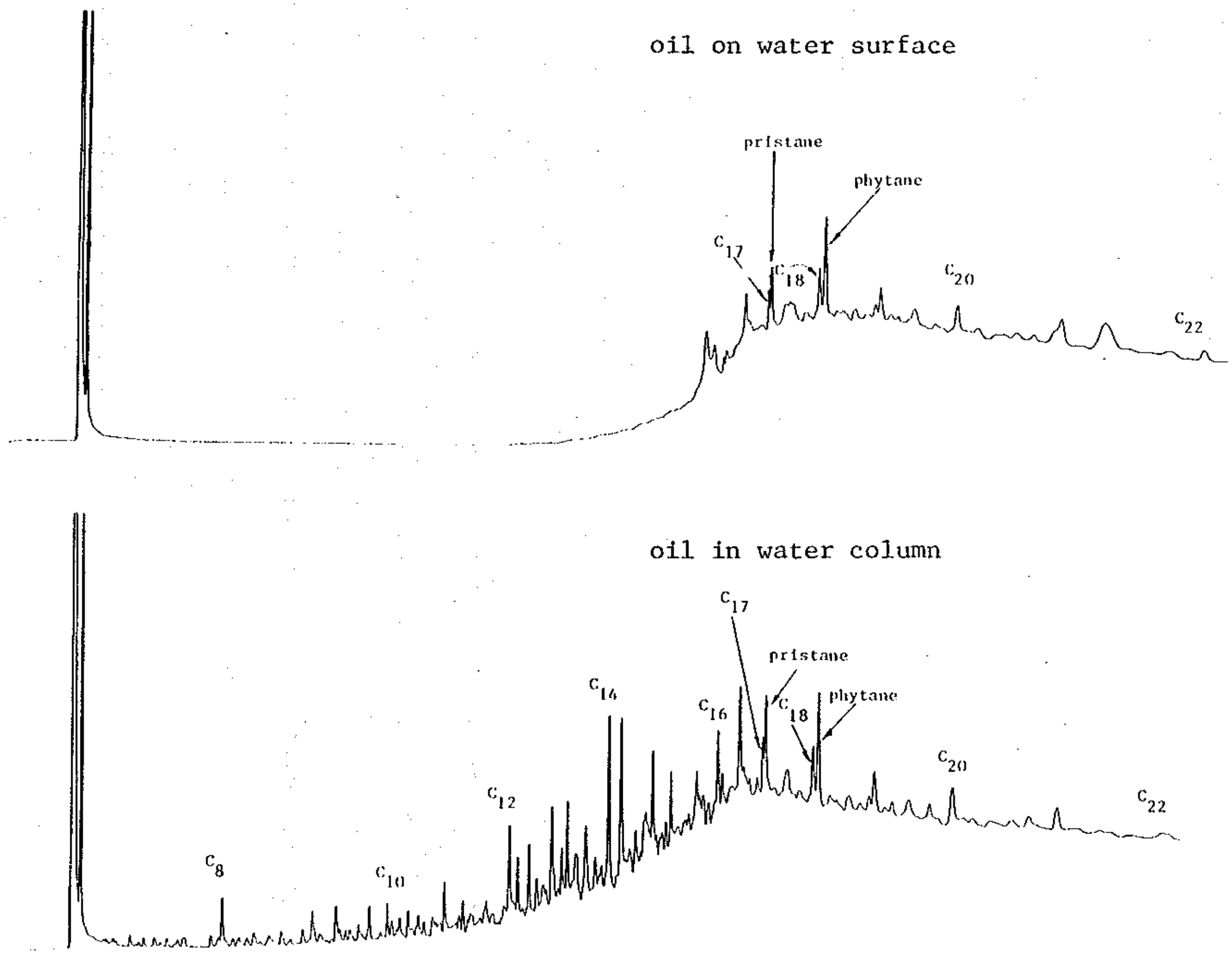

Figure 12. Long-term weathering of California Crude API 15 after 5 months.

The new oil matrix amounts can then be calculated and an overall composition deduced. The overall oil vapour pressure and solubility can be estimated. If densities and viscosities can be assigned to each element, the overall oil density and viscosity can be deduced.

The overall aims of the modelling effort are then to

- determine which element definition is most appropriate from the analytical and modelling viewpoints, and the optimal number of elements;
- express the initial oil composition in terms of element amounts;
- conduct weathering experiments to obtain changes in oil composition and properties;
- assign partition coefficients, densities and viscosities to each element;
- reconcile the model results with the experimental data, and in doing so develop appropriate "mixing rules", especially for viscosity.

A fascinating, important and difficult issue is that of "crust" formation. It should be straightforward to use the model to estimate weathering of the crust, although it may be necessary to include allowance for photolysis. The effect of the crust is believed to be to retard exposure of the interior oil, that is , the oil is no longer well-mixed. We envisage that the model will calculate a changing viscosity as a function of time. As the viscosity increases, oil mixing becomes less rapid, surface-to-bulk exchange is reduced, and eventually a near-immobile surface layer forms. This could be described by a two-compartment model (Figure 13) in which the surface-interior exchange rate is a function of viscosity and diffusivity. At early stages of weathering the exchange will be sufficiently rapid that near homogeneous conditions will exist, but as viscosity increases a heterogeneity will develop and grow. A major unresolved issue is how to express this exchange rate reliably. We believe that it should be possible to formulate a model and calibrate it with experimental data.

It will then be possible to estimate the density of the oil mass from a knowledge of the relative proportions of the crust and interior volumes. Finally, the equations should be capable of being used for estimation of oil weathering at sea (preferably using real spill observed data) and for incorporation into oil spill models.

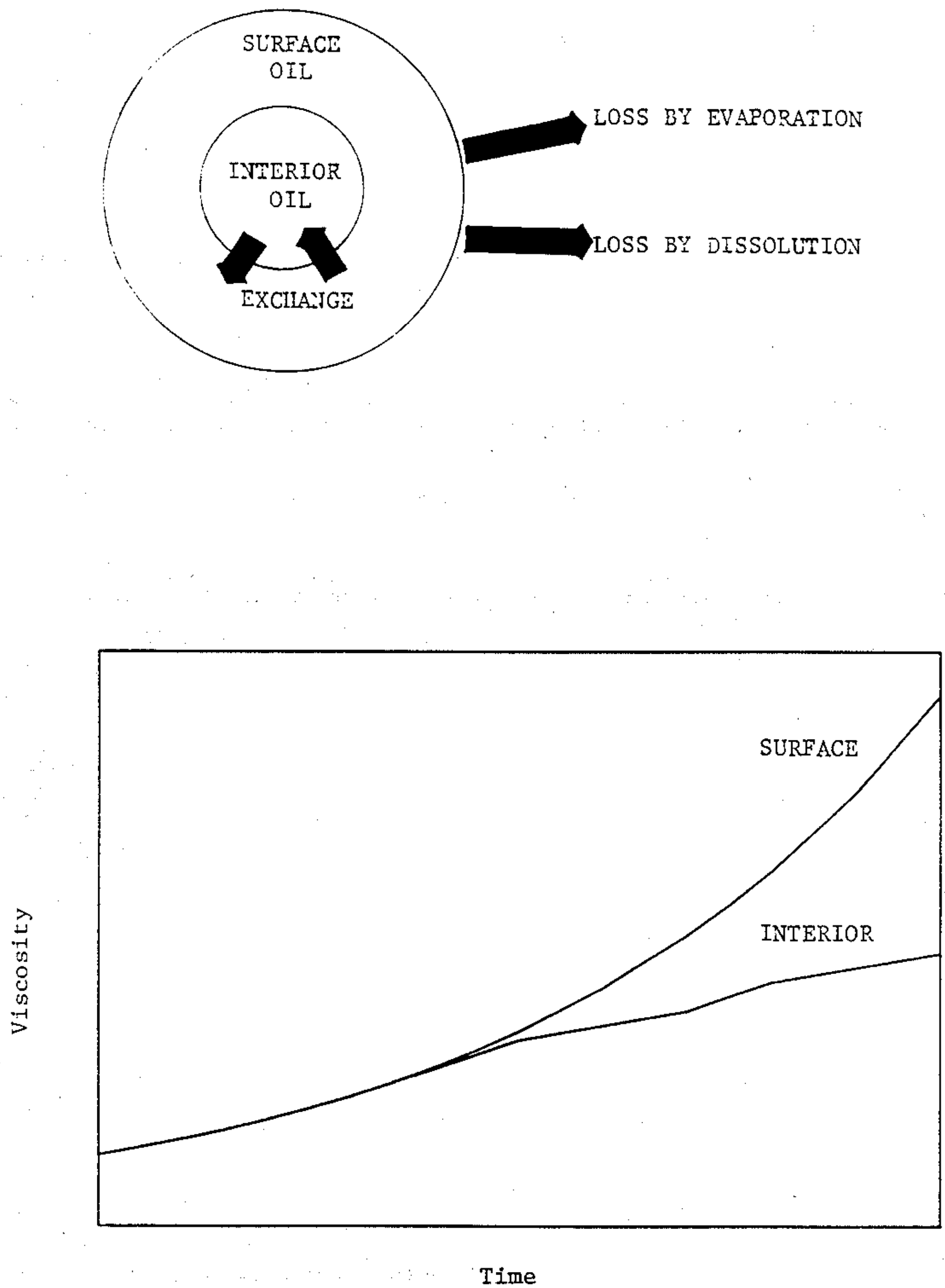

Figure 13. Two compartment model for "crust" formation.

CONCLUSIONS

The nature of the experimental program for determining the long-term weathering behaviour of heavy oils has been described and some illustrative results presented. The modelling approach by which the data will be processed has been outlined.

The first major unresolved issue is the optimal method by which the hydrocarbon mixture can be classified according to water solubility. When this is established it should be possible to estimate the magnitude of the matrix elements for each oil and test the models' validity against experimental data.

The second issue is the optimal treatment of "crust" formation, especially the crust thickness and exchange rates with the less-weathered interior oil.

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REFERENCES

Billington, J.W., G.L. Huang, F. Szeto, W.Y. Shiu and D. Mackay. 1988. Preparation of aqueous solutions of sparingly soluble organic substances: I. Single-component systems. Environ. Toxicol. Chem. 7:117-124.

Bobra, M.A. 1989. A Catalogue of Crude Oil and Oil Product Properties. Report EE-114. Environment Canada.

Cook, F.D. and D.W.S Westlake. 1976. Biodegradability of Northern Crude oil. Report No. QS-8116-000-EE-AI. Department of Indian and Northern Affairs, Ottawa.

Eastcott, L., W.Y. Shiu and D. Mackay. 1987. Weathering of Crude Oil in Surface Soils. Report from the University of Toronto for PACE (Petroleum Association for the Conservation of the Canadian Environment).

Lee, S.C., D. Mackay, F. Bonville, E. Joner and W.Y. Shiu. 1989. A Study of the Long-Term Weathering of Submerged and Overwashed Oil. Report EE-119. Environment Canada, Ottawa.

Mackay, D. 1987. Formation and Stability of Water-in-Oil Emulsions. Report EE-93. Environment Canada, Ottawa.

Payne, J.R. and C.R. Phillips. 1985. Petroleum Spills in the Marine Environment: The chemistry and formation of water-in-oil emulsions and tar balls. Lewis Publishers, Inc., Michigan.

Shiu, W.Y., A. Maijanen, A.L.Y. Ng and D. Mackay. 1988. Preparation of aqueous solutions of sparingly soluble organic substances: II. Multicomponent systems - hydrocarbon mixtures and petroleum products. Environ. Toxicol. Chem. 7:125-137.

Stiver, W. and D. Mackay. 1984. Evaporation rate of spills of hydrocarbons and petroleum mixtures. Environ. Sci. Technol. 18:834-840.